

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-3

Lecture-13

Greetings, I welcome you all to the twelfth lecture of this course and we have already begun the discussion on metallurgical waste recycling and we are going into the waste of aluminium industries. We are going to look at one of the most important waste that is generated in the aluminum industry, red mud production. Red mud is one of the most important and challenging wastes that are produced in the aluminum industry and why do we refer to it as one of the most challenging, we'll see that in today's lecture.

Red mud is generated during Bayer process after filtration of the leach liquor. In Bayer process, we are using the alkaline solution, sodium hydroxide and we leach it with the raw material that is the bauxite and after filtration of the leach liquor and leach liquor is of course, used for further processing, but when we are removing the residual solid, what we get exactly is the red mud. In that sense, residual solid is red mud of the Bayer process.

We know that the leach liquor will be used for further processing to make aluminium that will be produced in the Hall-Heroult process. But the red mud is generated in the Bayer process itself, a step well before we utilize alumina for Hall-Heroult process. Red mud is generated during the Bayer process. Nearly, 1 to 2 tons of red mud is produced per ton of alumina. If we have one ton of alumina, we can have one to two tons of red mud that is generated during the Bayer process which means the production of alumina and production of red mud is either almost equal or the production of red mud would be nearly doubled which means, we have large quantity of red mud just by assuming but what exactly is the figure? We can see that nearly 4 billion tons of red mud is already produced and, of course this is on a global scale, the rate of red mud production is nearly 180 million tons per year and why is this happening because the primary aluminium production also generates the red mud. And despite recycling of aluminum scrap primary aluminum production is on the rise basically. Even after using aluminium scraps, fresh

aluminium/virgin aluminium is still being produced which means the generation of red mud is not going to stop and of course this rate can increase if the production of primary aluminium keeps on increasing. Why is it so difficult to recycle or devise a treatment process? The complex phases and the complexity that is present in the red mud makes the treatment difficult.

And we will see that since red mud is produced during the leaching step of the Bayer process, the alkalinity that is the alkaline nature of red mud that is present in it makes it very difficult to handle.

(Ref. 4:55)

Red Mud Lecture #12

- Red mud is generated during Bayer Process after filtration of leach liquor
- Nearly \checkmark 1-2 tons of RM is produced per ton of alumina
- \checkmark 4 billion tons of RM is produced globally. 180 million tons/year production rate
- Complex phases present, making the treatment process difficult

Primary aluminium
production also generates
the Red Mud.

We will now look at the general composition of red mud and again we will see that the phases that are being described, the general composition that we are seeing here are again collected from some references and there is a fair chance that the red mud collected from a given aluminum industry can have some phases and some compositions that are outliers. It is fairly possible that the red mud composition can change from sample to sample, from industry to industry, from Bayer process unit to Bayer process unit. Let us just look at the important phases. Al_2O_3 -aluminum oxide, magnesium oxide, silica, CaO , Fe_2O_3 , K_2O , Na_2O and to our surprise TiO_2 as well. TiO_2 is coming from the raw material that we are using in the Bayer process.

Nearly 10 to 30% Al_2O_3 , 10 to 20%, nearly 20%. The alumina is relatively limited to nearly 20 to 30%. Similarly, silica can range from 20 to 30%. Calcium oxide can range from nearly 2 to 20%. Iron is one of the most important phases.

It is around 60% at times it is around 30% or 20%. Sodium oxide can range to around 2 to 12%. And TiO_2 again depends upon what type of raw material is being used. We can have 10 to 15% or even negligible amount of TiO_2 . This depends upon what type of raw material is being used.

But it is consistent that large quantity of iron oxide is present. And since, we have Al_2O_3 , MgO , CaO , K_2O , Na_2O , we see that the presence of these phases makes it very complex. It's not just a single phase material. It is a multiple phase material with iron oxide, aluminum oxide, silica and calcium being one of the dominant phases and not only just that these phases are present

in some of the red mud samples, rare earth elements have also been identified. Rare earth elements have also been characterized in the red mud sample which means that and of course we know that the composition of the red mud, the rare earth elements in the red mud is relatively very less. This could be present in parts per million or other, the composition basically fluctuates from sample to sample. But this has led to development of processes that are focused on REE only.

Basically rare earth extraction from red mud. These types of processes have also been investigated. These are being explored on various scales, laboratory scales, pilot scales. And other routes, other major routes will now be discussed. Hazardous nature of red mud.

When a large variety of phases are present and we have iron oxide, aluminum oxide, magnesium, calcium oxide, sodium oxide, we can see that it becomes very complex and it is highly alkaline waste.

(Ref. 9::13)

General composition

Important phases							
Al_2O_3	MgO	SiO_2	CaO	Fe_2O_3	K_2O	Na_2O	TiO_2
10-30	0-1	3-30	2-20	15-60	0-3	2-12	-
10-20	-	3-20	2-8	~30	-	2-10	10-15
21	-	18	14.9	19.7	-	6.9	3.3

(Wu et al. 2006, Lingxiang et al 2004, Wang et al. 2004)

Some rare earth elements have also been identified in Red Mud in trace quantities

What normally happens is people collect red mud, they let it settle, they remove the liquid that percolates through it and reuse it because it is highly alkaline and this liquid could be reused but even after that when the liquid is completely drained out still red mud has highly, high alkaline content and this is the reason why storage itself is difficult. Storage becomes difficult to environmental hazards. We've already mentioned that. Highly alkaline waste. Solid and groundwater contamination.

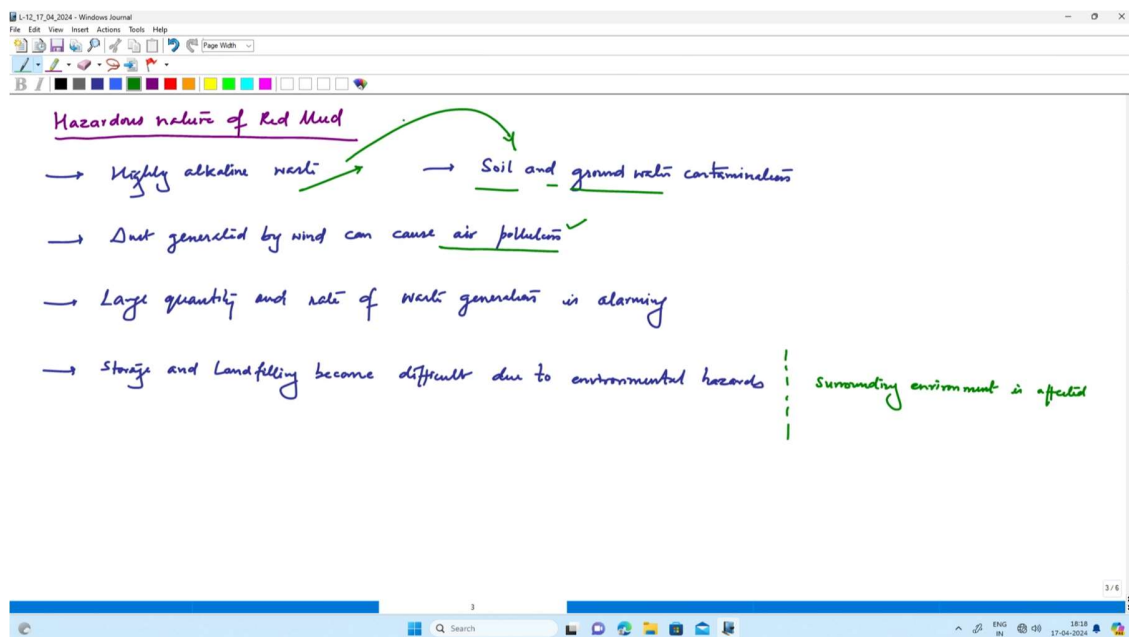
If we think of considering it as waste that we can just simply dump in dump yards and landfills, the soil and groundwater contamination is bound to happen. Not only just that, we have if the dust particles, if they're red mud is coming in contact with dust particles and some dust can be blown away from these piles, these large stockpiles of red mud. It can also cause air pollution.

Not only is groundwater and soil getting polluted, air pollution is also observed. Large quantity, sheer quantity, the quantity that we have seen nearly 4 billion tons of red mud we've already seen and the production rate itself if it is nearly around 150 to 180 million tons per year the production rate is also not dropping. So, the sheer quantity itself, the large quantity of red mud and on top of that the quantity, the red mud production rates are alarming. It is very important to devise good recycling strategies. Since it's a big challenge and the composition and high alkalinity of red mud have been described as the major hurdles that stop the red mud recycling. People have devised large wide variety of

recycling strategies that could be used to recycle red mud. Storage and landfilling become difficult due to environmental hazards.

We've already seen soil and groundwater contamination air pollution, which means the surrounding environment is affected. The ground may become unusable, the ground water may become unusable and the air itself may get contaminated due to the fine particles of the red mud.

(Ref. 12:45)



Methods of recycling red mud. What are the key methods that are used for recycling red mud? Wide variety of processes have been developed. We've already seen in the previous slide, we were discussing what are the challenges. The complexity of the raw material, the red mud and the phases that are present in it on top of that, the high alkaline nature, highly alkaline nature of the raw material this makes it a big challenge. Wide variety of processes have been developed for recycling metallic values from red mud. And we see that the first choice that people would go for is the iron that is present in the red mud. Carbothermic roasting using coke can help in recovering iron concentrate with nearly about 90% recovery. And it could be around 1150 degree Celsius.

The other method could be high temperature reduction. Again at 1150, we can get pig iron with about 93 percent recovery. It is possible to produce various iron rich products,

not just pig iron, you can think of making alloys. Let's say, iron-nickel alloys or some other alloys so iron rich products but there are other methods as well.

People have thought of using vacuum reduction or maybe hydrogen reduction and other roasting technologies that could be employed on red mud so that various iron rich products can be produced.

(Ref. 14:45)

Methods of Recycling Red Mud

→ Wide variety of processes have been developed for recycling metallic values from red mud.

- carbothermic roasting using coke \rightarrow Iron concentrate in 90% recovery (1150°C) \rightarrow Iron-rich products
- High temperature reduction \rightarrow pig iron in 93% recovery (1150°C) \rightarrow Iron-rich products

→ Vacuum reduction and other pyrometallurgical process have been used.

Mostly, when we think of pyrometallurgical processes they would be targeting the metallic values directly and predominantly they would go for iron recovery. And the one of the reasons why red mud is called red mud is because of the high iron content that is present in it.

An obvious choice that most people would try and recover the metallic values from the red mud. When we think of hydrometallurgical processes we can have a wide variety of schemes because hydrometallurgical processes normally would just take raw material. Again in this case just we are using red mud as a raw material, we are again assuming that it is sorted, classified, categorized and pre-treated. If red mud is pre-treated, we can go ahead with it. The first step

would be leaching and we can have other processes and we can get products. We have leaching, precipitation, solvent extraction as the processes that support the leach liquor and using that it has been reported that nearly about let us say 25 to 65 percent aluminium is produced, 20 to 90 percent of iron is produced, 5 to 80 percent of titanium. If titanium is present again, this depends upon whether titanium was present in the raw material or not.

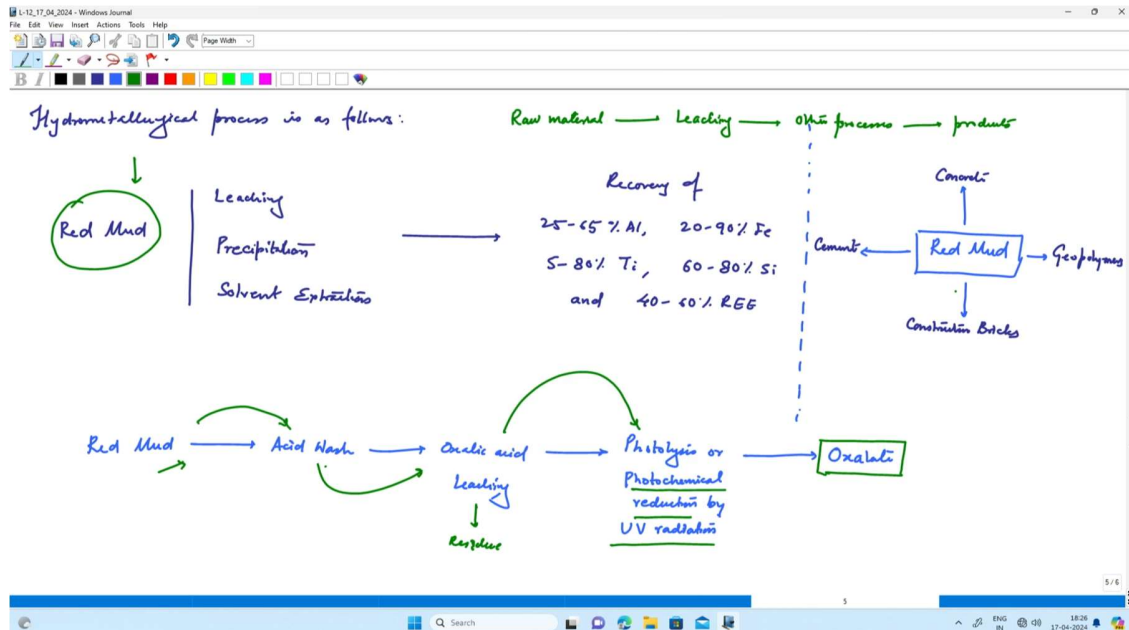
Again that depends upon the presence of titanium in bauxite. If the bauxite had titanium, it would, it can be recovered from red mud as well. Titanium, 5 to 80%, 60 to 80% silicon, 40 to 60% of REE. REE means the rare earth elements if they are present and it is seen that in the composition of red mud if REE is relatively very less and nearly 40 to 60 percent of the REE

that is present in the red mud can be recovered. The other processes and taking an example we can see that another hydrometallurgical example we can just see where in red mud is acid washed. Why are we washing it with acid? It is fairly possible to directly use water. But acid wash basically helps in neutralizing the alkalinity.

The alkaline nature of red mud is being balanced by acid wash. And oxalic acid leaching is done after that. When we know that the red mud is neutralized, we can go for oxalic acid leaching. And we have the residue, red mud residue which could be basically reused as a raw material for some other purpose and upon characterization,

the leach liquor however could be subjected to UV radiation. So, when we go for UV radiation, it leads to photochemical reduction. We are seeing here is the steps that are followed to make the oxalate product in the end. And we see that first it was acid washed to make it neutral and after that oxalic acid was used and leach liquor was used for photolysis, photochemical reduction by subjecting it to UV radiation and we finally, get the let us say ferrous oxalate or other products. Generally, we can also see that red mud can be used as raw material for making concretes, construction bricks, geopolymers and cements.

(Ref. 19:55)



People have tried to use it as raw material for construction applications as well. They would like to pretreat the raw red mud in such a way that it does not react with other materials, but these are the methods by which the recycling of red mud has been described. We'll now try to summarize what we have learned in today's class.

Red mud is one of the most hazardous materials that have been posing a challenge in the aluminium industry. The production rate itself of red mud is very large. The quantity that has been produced itself is also a big challenge. We have huge stockpiles of red mud that require good recycling strategy and we know the complexity of the raw material because the multiple phases are present in various composition various chemical compositions and recovery of valuable materials, let's say iron or aluminum or titanium or other metallic values becomes very big a challenge. Pyrometallurgical as well as hydrometallurgical processes have been described and in the recent years people have been extensively exploring the possibilities of developing good recycling strategy for red mud. It is being done as we speak and the challenge is to make red mud a good raw material for recycling and we've also seen that it can be used as a raw material for construction applications. Some sort of pretreatment is essential before it is used in such applications. In the upcoming classes, we will be continuing more on the aluminium industrial wastes. Thank you.